Artificial Bristles from Proteins

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A method is described for producing coarse fibers from casein by extruding a heated mixture of casein and water through a suitable die. When the fiber is stretched and hardened, under tension, with quinone, a bristle material is obtained, which is being tested in certain types of brushes.

METHODS for the conversion of amorphous proteins into fibers have long been known. In 1898 Millar (*3*) prepared protein fibers by extruding heated protein-water mixtures into air. A few years later Todtenhaupt (*6*) made casein fibers by extruding an alkaline solution of casein into an acid bath. Recent improvements in the latter process have resulted in the commercial development of a textile fiber from casein. Early in the development of protein fibers, it was found that the durability of the fiber was markedly increased by treatment with formaldehyde and other tanning agents. These substances decrease water absorption and bacterial decomposition of protein fibers and make them more flexible. Water absorption of the treated protein fiber is not completely eliminated, however, and loss in strength and shape of the fibers in the presence of water limits their use.

The present shortage of pig bristles and other coarse animal hair, such as horsehair, suggested the development of a protein fiber having the size and properties of these natural hairs. In the following method for preparing such fiber, heated isoelectric protein mixed with water is extruded into air; it is then stretched and hardened, under tension, with quinone alone or quinone followed by formaldehyde.

PREPARATION OF FIBERS

A number of proteins, including casein, soybean, gelatin, zein, edestin, arachin, and glutenin, have been converted into fibers by extrusion. However, casein was used entirely in the development of fibers suitable for bristle material as described in this report. Several commercial acid-precipitated caseins were found to be suitable for fiber extrusion. Purification of the better commercial caseins did not materially improve the quality of the fiber. The quality of the casein, however, is of importance for making fiber. To be suitable for the production of fiber, a casein should be free from lactose and other whey constituents, be soluble in borax solution, and yield an aqueous extract having a pH near the isoelectric point of 4.7.

In making casein fiber, 40-100 mesh commercial acid-precipitated casein containing approximately 9% moisture is mixed with 70% of its weight of water, and the mixture is allowed to stand for an hour. The hydrated casein is placed in a discontinuous press of the cylinder type with a volume of 370 cc. (Figure 1 and 2) and heated slowly to about 95° C. to remove air and form a plastic mass. Fibers are formed by forcing the heated casein-water mixture through a die with holes of a suitable diameter, usually from 0.3 to 0.6 mm. A finely woven stainless steel screen or breaker plate is placed in back of the die to assist in the removal of air and foreign material from the casein before the fiber is formed. To minimize sticking, the fibers are passed rapidly by means of rotating drums through a solution, at a pH of about 4.7, containing 2% formaldehyde, 0.1% naphthalene sulfonate, and 10% sodium sulfate. The fibers are collected on a suitable reel,

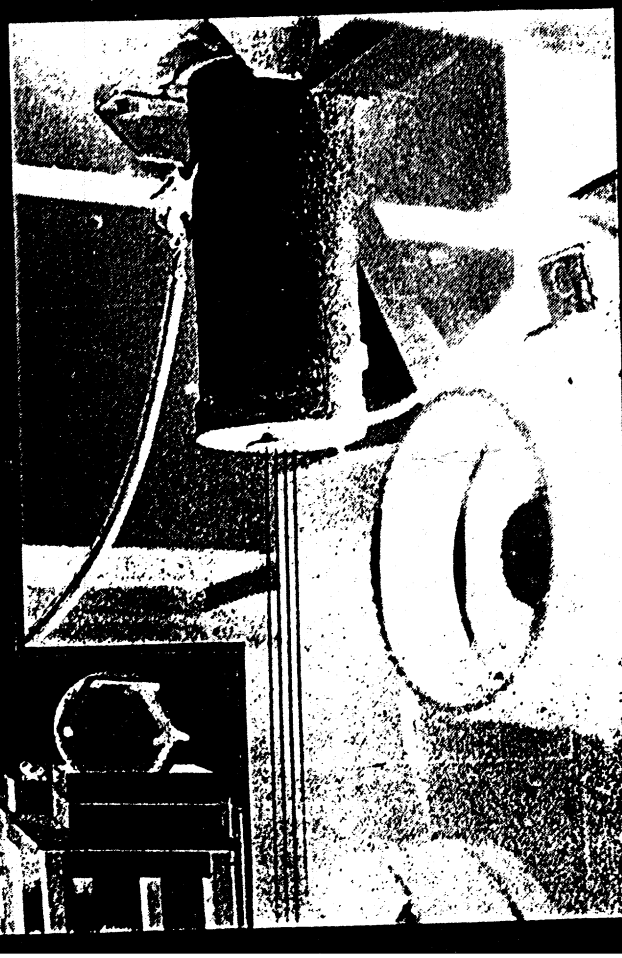
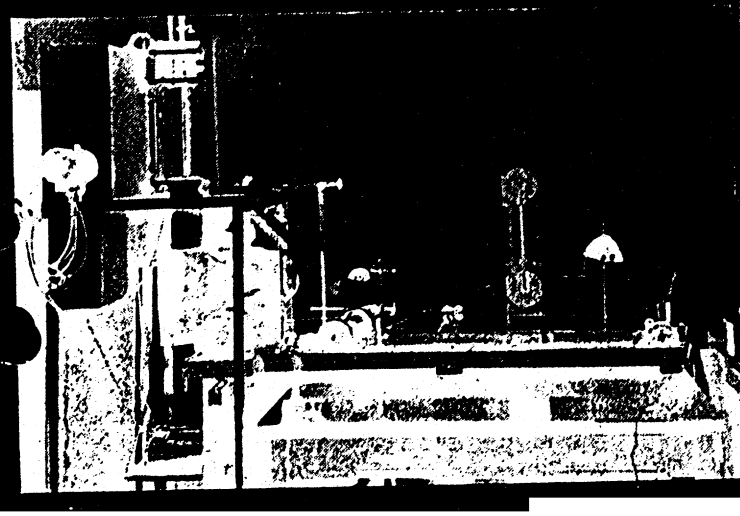


Figure 1 (*Below*). Press and Accessory Equipment for Spinning Casein Fibers

Figure 2 (*Right*). Close-up View of Fiber Formed by Extrusion of Heated Casein-Water Mixture through the Four-Hole Die into Air



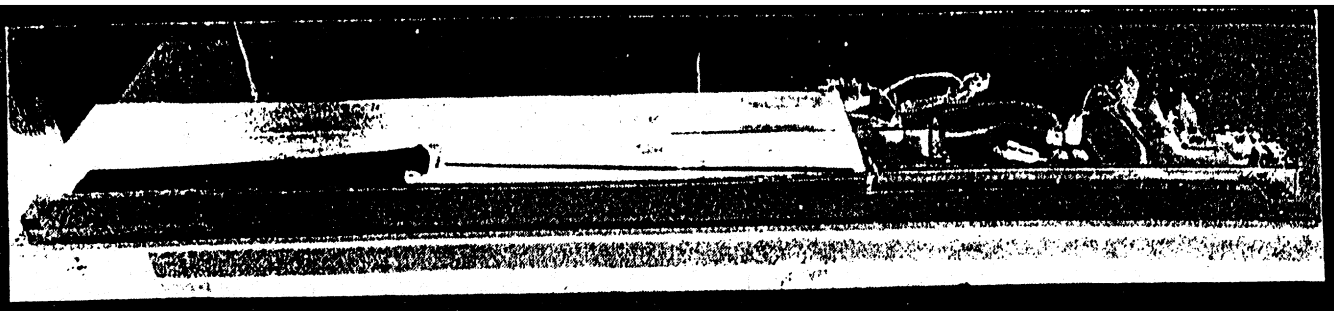


Figure 3. Motor-Driven Machine for Stretching Skein Casein Fiber during Hardening with Quinone

as shown in Figure 1. Fiber can also be made by extruding casein mixed with only 37% of its weight of water. In this case sticking is so much reduced that the fibers are extruded directly in air without the bath.

The extruded fiber, in the form of a skein of continuous filaments, is placed in the stretching bath (Figure 3) and is passed through two stirrups. One of these is stationary while the other is gradually pulled along the length of the tank by a motor mechanism. When a saturated solution of quinone is employed at room temperature, the fiber is stretched at the rate of 1% of the original length per minute until the original length has been doubled; the time required is 1 hour and 40 minutes. When higher temperatures are used, the rate of stretching must be increased. After stretching is completed, the fiber remains under tension in the quinone bath (room temperature) for at least 24 hours; further hardening and attendant reduction of water absorption may be obtained by allowing it to stand under tension in a 2% formaldehyde solution for another 24 hours. Hardening has been found to be best near pH 4.7. Finally the fiber is removed from the bath, washed, and dried at room temperature under sufficient tension to keep it straight.

The effect of variations in degree of stretching on tensile strength and flexibility is shown in Figure 4. The testing was done at 65% relative humidity and 70° F. on a standard Scott inclined-plane serigraph-2 testing machine. The tensile strength of a fiber with a loop tied in it was employed as a measure of flexibility (curve *C*). As the degree of stretching is increased, tensile strength increases. However, a point is reached where an increase in the degree of stretching reduces flexibility. Consequently, stretching is not carried to the greatest possible extent in making bristlelike casein fibers. Instead the fibers are stretched only to twice their original length in the quinone bath in order to obtain the highest strength consistent with greatest flexibility. Stretching also increases the wet strength and slightly decreases water absorption. This treatment results in a casein bristle with a dry strength of 0.7–0.8 gram per denier under standard conditions and a wet strength of 0.3–0.4 gram per denier after immersion in water for 4 hours at 70° F. (Table I).

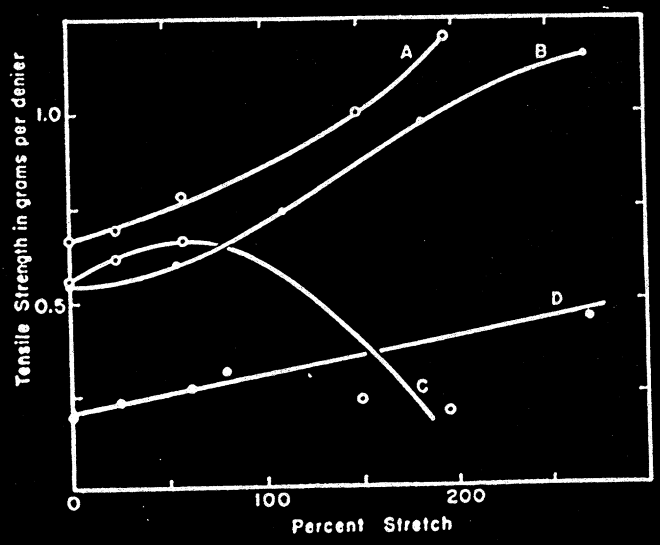


Figure 4. Influence of Degree of Stretching on Properties of Fiber (300–1000 denier)

A and *B*, dry tensile strength; *C*, tensile strength of fiber with a loop tied in it (flexibility); *D*, wet tensile strength

PROPERTIES AND USES OF ARTIFICIAL BRISTLES

The stretched and quinone-hardened casein fibers are cylindrical (Figure 5) and black. Figure 6 shows samples of experimental brushes made with casein bristle fiber. The stiffness of the fiber varies with the diameter. Fibers with a diameter of 0.6 mm. (3312 denier) are quite stiff; fibers with a diameter of 0.2 mm. (368 denier) are soft and pliable. Experimental paint brushes made with this fiber have been prepared in considerable numbers. Since heating hardened casein fibers above 100° C. for several hours produces brittleness, ordinary methods of setting natural bristles such as that involving the vulcanization of rubber for several hours at 140° are unsuited for artificial bristles made from casein. This difficulty has been overcome by vulcanizing with rubber at lower temperatures and also by using a setting ma-

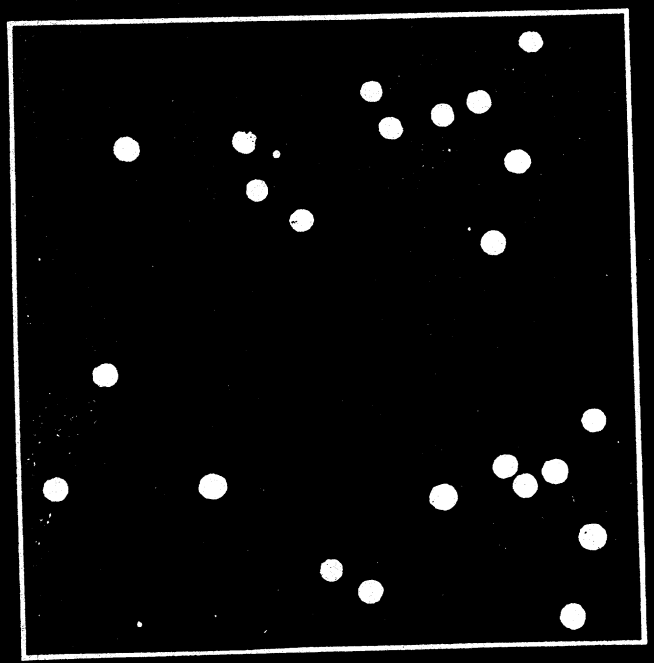


Figure 5. Photomicrograph of a Cross Section of Casein Bristles (× 11)

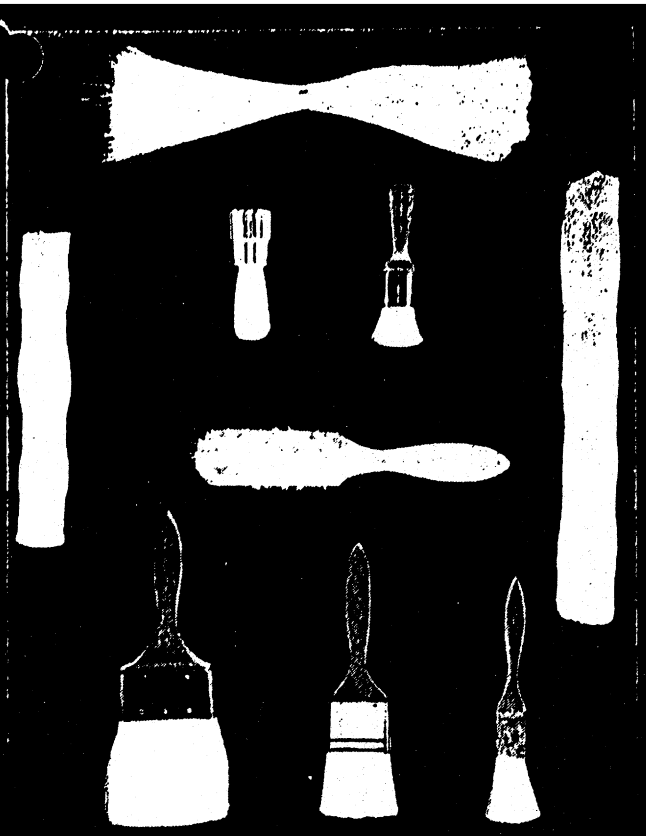


Figure 6. Casein Bristle and Experimental Brushes Made from Artificial Fiber

terial, made of urea-formaldehyde and alkyd types of synthetic resin, that hardens at 80° C. These paint brushes, although made of untapered bristles, have good paint-carrying capacity, make smooth films, and have good wear resistance. The bristles are resistant to oils and fat solvents, but soften when allowed to stand in water.

Although the dry tensile strength of the casein bristles is not so great as that of natural bristles, the strength is adequate for most brushes not subject to wetting with water. In water the casein bristles absorb about 18% water, become soft, and have a tensile strength of only about half their dry tensile strength; this makes them unsuited for use in water. Table II compares casein bristles with natural bristles.

TABLE I. STRENGTH OF STANDARD CASEIN BRISTLES STRETCHED TO TWICE THEIR ORIGINAL LENGTH

Expt. No.	Denier	Tensile Strength, G./Denier[a]	
		65% r.h., 70° F.	4 hours in water
40	214	0.84	0.36
		0.78	0.48
		..	0.33
67	470	0.85	0.44
		0.76	0.42
		0.76	0.37
104	425	0.71	0.47
		0.79	0.40
		0.86	0.45
388	507	0.71	
		0.71	
		0.73	
443	421	0.73	
		0.80	
		0.82	

[a] Grams per denier can be converted to pounds per square inch by multiplying by the factor 16,630 since the fiber has a density of about 1.3. [Sieminski, M.A., *Rayon Textile Monthly*, 24, 63 (1943)]. Denier = weight in grams of 9000 meters of fiber.

Casein bristles are stable in air under ordinary conditions and have been kept for two years without deterioration. Even after long heating at 60° C., the physical properties of the fiber were changed only slightly when subsequently conditioned at room temperature.

TABLE II. COMPARISON OF CASEIN BRISTLES WITH NATURAL BRISTLES

Material	Tensile Strength, G./Denier			% Water after 24 Hr. in Water (22–25° C.)
	65% r.h., 70° F.	Single knot	4 hr. in water	
Casein bristle	0.7–0.8	0.6–0.65	0.35–0.45	18.5
Pig bristle	1.0–1.2	0.8–0.9	0.9–1.2	20
Horsehair	1.2–1.4	0.9–1.0	1.0–1.3	21

DISCUSSION

The batch process described for the production of casein bristles is adequate for many purposes. For large-scale economic production, however, a continuous process would be highly advantageous, and it has been found that the fiber can be extruded with a commercially available screw-type extruder. The process described here, involving hardening for 24 hours at room temperature, produces a fiber containing approximately 10% quinone. This amount of quinone is required to make the fiber durable and resistant to water. The influence of temperature on the rate of uptake of quinone is shown in Figure 7. In order to obtain approximately 10% quinone in the fiber in 10 minutes, it is necessary to use a temperature of 60° C.

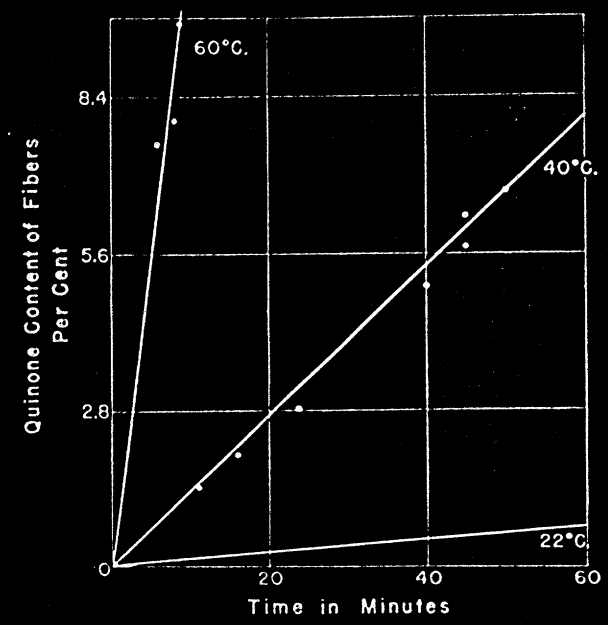


Figure 7. Influence of Temperature on Uptake of Quinone (Fiber Diameter 0.3–0.5 Mm. or 828–2301 Denier)

The simultaneous stretching and hardening of the fiber in a relatively short period requires further investigation. To increase the tensile strength of the fibers, the stretch must be applied at a definite time during hardening. Considerable stretch can be applied to the fiber as it emerges from the orifice of the extruder while it is in the air and still at an elevated temperature. However, no added strength is given the fiber by the maximum stretch that can be applied in this manner. It is necessary to have a certain minimum degree of hardening in order to increase the strength by stretching. If the hardening has progressed too far, however, the fiber can be stretched comparatively little before

it breaks. There is thus an optimum amount of hardening for permitting the maximum effective stretch to be applied. This was shown by an experiment in which the maximum degree of stretch that could be applied to the fibers was determined at 5-minute intervals after immersion in a quinone solution under various conditions. The maximum extension of about 300% was attained in 30 to 45 minutes at 22°, 15 to 35 minutes at 35°, and 10 minutes at 50° C. in 1% quinone, but it was attained in less than 5 minutes at 50° in 2% quinone. Stretch should be applied under any of these combinations of temperature and time to be of most benefit. If the fiber is to be stretched not more than 100%, however, there is considerable latitude in the time at which stretch may be applied.

The reaction of quinone with casein appears to be irreversible in neutral solutions. Casein fiber hardened with quinone is superior to formaldehyde-hardened fiber with respect to brittleness and resistance to water. Quinone hardening was most effective near the isoelectric point of casein. Although the nature of the reactions is still unknown, quinone has been found to react with proteins and many amino compounds (*1*, *2*); most of these reactions proceed readily in aqueous solution at room temperature. It has been found (*4*, *5*) that deaminized collagen (hide powder) fixes about 60% of the amount of quinone fixed by untreated collagen in 24 hours. It is thus probable that the ε-amino groups of lysine are available in proteins for reactions of this type, but that they account for only part of the reaction.

The modification of casein by acetylation, deamination, or esterification, as well as the addition of small quantities of quinone or formaldehyde, markedly decreases the ability of casein to form fibers in the presence of water.

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